Molybdenum(VI) Complexes from Diols and Aminoalcohols: the Occurrence of MoO_2, Mo_2O_3, and Mo_2O_5 Core Structures

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The co-ordination behaviour of molybdenum(VI) towards diols and aminoalcohols is discussed, particularly in relation to newly determined reference structures. A pinacol (H_2pin) complex, typical of the yellow vicinal diol derivatives, is constituted $[MoO(pin)(Hpin)]_2O$, with an Mo_2O_3 core. An Mo_2O_5 core is present in the anion $[\{MoO_2(Hnta)\}_2O]^{2-}$, formed by nitrilotriacetic acid (H_3nta) at low pH. Several new complexes in which ligand bridging is inferred have been prepared. One of these, $[\{MoO_2(Hpin)(OMe)\}_2]\cdot 2MeOH$, which is derived from the yellow pinacolate, is shown by *X*-ray analysis to have methoxy-bridging. The bridge vibration from an Mo_2O_3 core is close to 750 cm^{-1}, but the pattern of bands from an Mo_2O_5 core is variable. The $MoO_{lb}Mo$ vibration involving an oxygen bridge provided by a chelating ligand gives an i.r. band in the region 625—650 cm^{-1}.

THE capacity of a molybdenum(VI) centre to develop six-co-ordination towards oxygen through use of different combinations of terminal, O_t, core-bridging, O_b, and ligand, O_l, oxygen atoms is well known.[1,2] In addition, there may be bridging by ligand oxygen, O_{lb}. The type of molybdenum–oxygen core with which a polydentate ligand co-ordinates is determined in part by the match between the ligand configuration and alternative core structures. For example, at low pH (*ca.* 2) uramildiacetic acid $\overline{\text{CO-NH-CO-NH-CO-C}}\text{H-N}(CH_2CO_2H)_2$ functions as a quadridentate ligand which co-ordinates as the trianion (uda^{3-}, derived from the enolic form) to give a complex $[MoO_2(uda)]^-$ with a *cis*-dioxo-MoO_2 core.[3] On the other hand it is now found that at the same pH nitrilotriacetic acid, $N(CH_2CO_2H)_3$ (H_3nta), forms complexes of the kind $[Mo_2O_5(Hnta)_2]^{2-}$, having an Mo_2O_5 core. Provided the structures of reference compounds are known, i.r. spectra can in simple cases enable identification of the type of core in a compound of undetermined structure.[4] The applicability of this approach is necessarily dependent upon identification of the (usually strong) Mo–O_t and Mo–O_b bands among the ligand bands, and to this end Newton and McDonald [5] have made careful assignments of $\nu(MoO_bMo)$ frequencies in various molybdenum complexes containing thio-ligands. In examining the co-ordination behaviour of several diols, aminoalcohols, and other ligands which might be expected to produce molybdenum(VI) complexes of varied types, including examples with ligand bridging, we have gained further information on the applicability of i.r. assignments for identification of molybdenum–oxygen core structures.

RESULTS AND DISCUSSION

The compounds are considered within four classes. (*i*) Compounds of the type $[MoO_2(HL)_2]$ (from ligand H_2L) containing the *cis*-dioxo-MoO_2 core associated with two monodeprotonated ligands.[6] (*ii*) Yellow vicinal diol derivatives which are now shown to be of the type $[Mo_2O_3(HL)_2L_2]$, with an $O_tMoO_bMoO_t$ core, the generic structure having been established by an *X*-ray analysis of the complex formed by 2,3-dimethylbutane-2,3-diol (pinacol, dianion pin^{2-}). An i.r. vibration, $\nu(MoO_bMo)$ at *ca.* 750 cm^{-1}, is characteristic of this Mo_2O_3 core. (*iii*) A class having an Mo_2O_5 core, $(O_t)_2MoO_bMo(O_t)_2$, typified in the present work by the nitrilotriacetato-complex formed at low pH, as in the salt $Na_2[Mo_2O_5(Hnta)_2]\cdot 8H_2O$. (*iv*) A variety of ligand-bridged compounds, often containing a *cis*-dioxo-group, but for which the requirement of six-co-ordination would necessitate O_{lb} bridging.

Pairs of compounds of classes (*i*) and (*ii*) can in some cases be interconverted through reversible hydration and dehydration.[7,8] For the pinacolates, which have been examined in the present work, the interconversion can be represented as in the equation. In principle, this kind

$$2[MoO_2(Hpin)_2] \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} [Mo_2O_3(Hpin)_2(pin)_2]$$

of interconversion could, with suitable ligands, be expected to extend also to Mo_2O_5 and MoO_3 core structures.

Class (*i*).—Vicinal diols, *e.g.* ethylene glycol [6] (monoanion Heg^-) and propane-1,2-diol (monoanion Hpd^-) yield *cis*-dioxo-complexes [(1) and (2) respectively] of the type $[MoO_2(HL)_2]$ through co-ordination of two monodeprotonated ligands. In the crystalline glycolate there is strong intermolecular hydrogen bonding.[6]

There is a similar co-ordination around the molybdenum centre in the crystalline butane-2,3-diol (dianion bd^{2-}) compound, $[MoO_2(Hbd)_2]\cdot 2H_2bd$ (3), but the system of hydrogen bonds extends through a pair of intervening solvate molecules.[9] In the formation of this compound there is selective utilisation of isomeric molecules of the reactant butanediol, in the processes of both co-ordination and crystallisation. Within the crystal there are rows of molecules of the complex (each of symmetry C_2) parallel to the *a* axis (ref. 9, Figure 4, in which the *a* axis runs vertically down the page). The molecules in each row are related by centres of inversion to molecules in adjacent rows. Thus the molecules within any particular row contain ligands which are exclusively of one configuration, with the bis(*RR*) and bis(*SS*) types in alternate rows. These bis(*RR*) and bis(*SS*) ligands are associated with Δ and Λ absolute configurations respectively. The hydrogen-bonded solvate diol molecules are entirely of the *meso* (*RS*) type.

When heated under vacuum this butanediolate loses both the solvate molecules and water, the latter arising from inter-ligand degradation of hydroxyl groups. The resulting yellow product (4) shows an i.r. absorption at 750 cm^{-1}, indicative of an MoO_bMo bridge as in the class (*ii*) structure, *i.e.* $[Mo_2O_3(bd)_2(Hbd)_2]$.

TABLE 1

Infrared bands (cm^{-1}) of compounds

Compound	$\nu(Mo{-}O_t)$ [a]	$\nu(MoO_bMo)$	$\nu(Mo{-}O_l)$
(1) $[MoO_2(Heg)_2]$	948, 920		569m, 543s
(2) $[MoO_2(Hpd)_2]$	950, 920		620s, 547s, 485m
(3) $[MoO_2(Hbd)_2]\cdot 2H_2bd$	935, 921		610m, 538m
(5) $[MoO_2(mea)_2]$	900, 880		560s, 530m
(6) $[MoO_2(Hdea)_2]$ [b]	915, 883		565s, 545m
(8) $[MoO_2(Hpin)_2]$	900, 887		620m, 560m, 495m
(4) $[Mo_2O_3(bd)_2(Hbd)_2]$	950, 920	750s	625s, 550m
(7) $[Mo_2O_3(pin)_2(Hpin)_2]$	950	762m	610s, 500m
(10) $Na_2[Mo_2O_5(Hnta)_2]\cdot 8H_2O$	915	790s, 777s	567w, 530m
(11) $K_2[Mo_2O_5(Hnta)_2]\cdot 4H_2O$	925, 910	775s	510m,br
(12) $[NH_4]_2[Mo_2O_5(Hnta)_2]\cdot 4H_2O$	932, 916	780s	515m,br
(13) $[Mo_2O_5(aae)_2]$	882 (845, 825)	745s, 760 (sh)	610m, 565s, 485s
(9) $[\{MoO_2(Hpin)(OMe)\}_2]\cdot 2MeOH$	920, 895	690s [c]	570s, 560 (sh)
(14) $[\{MoO_2(npg)(OH_2)\}_2]$	957, 910	642m [c]	510m
(15) $[\{MoO_2(tmoe)\}_n]$	940, 885	635m [c]	600m, 550m
(16) $[\{MoO_2(deg)\}_n]$	945, 912	847s [b]	590s, 560w

[a] Strong bands. [b] A small quantity of product analysing as $MoO_2(dea)$, crystallised from one diethanolamine preparation after addition of ethanol. The compound gave bands at 912s, 892s, 835s, 589s, and 555w cm^{-1} in a spectrum closely similar to that from (16). [c] Ligand-bridged compound.

A monoethanolamine (monoanion mea$^-$) complex, $[MoO_2(mea)_2]$ (5), is of the same *cis*-dioxo-type. Moreover, the chief product from the Schultheis condensation reaction [10] between diethanolamine (dianion dea^{2-}) and molybdenum trioxide is again of this same type, *i.e.* $[MoO_2(Hdea)_2]$ (6). The i.r. spectrum of this product is compatible with co-ordination of the ligand $^-O(CH_2)_2NH(CH_2)_2OH$ through O and N, with the remaining OH group unco-ordinated but involved in hydrogen-bonding. Compounds (5) and (6) show closely similar $\nu(Mo{-}O_t)$ and $\nu(Mo{-}O_l)$ frequencies, indicative of similar co-ordination patterns.

Compounds of this $[MoO_2(HL)_2]$ type commonly show medium to strong bands, additional to any ligand bands, in the range 520—570 cm^{-1}, and sometimes to 620 cm^{-1} (Table 1). These bands are attributed to those $\nu(Mo{-}O_l)$ vibrations involving the more strongly bonded ligand atoms.

Class (*ii*).—A wide range of yellow compounds, to which the yellow butane-2,3-diolate (4) must belong, has been reported as forming in preference to the mononuclear *cis*-dioxo-type when one or both of the carbon atoms of the chelating chain in the vicinal diol are tertiary. A determination of the crystal structure of the yellow pinacolate (7) shows that the oxygen bridge of the OMoOMoO core is reinforced by two hydrogen bonds between pairs of ligands attached one to each molybdenum atom [11] (Figure 1). It seems reasonable to assume that all the yellow complexes formed by substituted glycols, with the characteristic MoO_bMo band close to 750 cm^{-1}, have essentially this same structure. Since the formation of the yellow compounds is reported to be promoted by increasing substitution, irrespective of the type of substituent, it can be suggested that the development of this structure with its intramolecular hydrogen bonding is favoured through steric inhibition of the development of alternative intermolecular hydrogen bonding. The formation of the yellow butane-2,3-diolate (4) indicates that the presence of two secondary carbon atoms is sufficient to promote the formation of a yellow derivative.

The susceptibility of the yellow complexes towards conversion into derivatives of other structural types is shown by the behaviour of the pinacolate. Crystallisation from a solution of the yellow pinacolate in ethanol in an open vessel (with access of atmospheric moisture) yields a colourless pinacolate, $[MoO_2(Hpin)_2]$ (8), of class (*i*). The same conversion occurs in methanol, but with

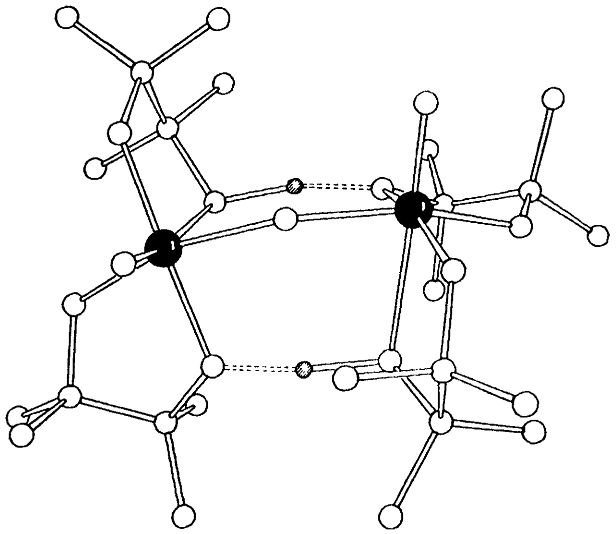

FIGURE 1 Co-ordination environment in the yellow pinacolate $[Mo_2O_3(pin)_2(Hpin)_2]$, showing the oxygen bridging and the intramolecular hydrogen bonding by the two hydroxylic protons. All skeletal atoms of the pinacolate ligands are shown as open circles

restricted access of moisture a methoxy-derivative $[\{MoO_2(Hpin)(OMe)\}_2]\cdot 2MeOH$ (9) is obtained. In this structure[12] two methoxy-bridges between molybdenum centres complete six-co-ordination, and unco-ordinated methanol is linked by hydrogen bonding to the pinacolate ligand.

Class (*iii*).—The nta^{3-} anion is known to function as a tridentate ligand[13] in salts of the type $M^I_3[MoO_3(nta)]$, which are formed at pH 6—7.[4] A second type of complex anion is now found to be produced by this ligand at pH 1.6. Determination of the structure of the sodium salt of this new series shows it to be $Na_2[Mo_2O_5(Hnta)_2]\cdot 8H_2O$, with the dianion $Hnta^{2-}$ still functioning as a tridentate ligand * through co-ordination of the nitrogen and of an oxygen of each of two carboxylate groups (Figure 2). The salts [sodium (10), potassium (11), and ammonium (12)] provide reference spectra from the rather uncommon Mo_2O_5 core,[14,15] with strong $\nu(Mo-O_t)$ bands at 910—930 cm^{-1} and $\nu(Mo-O_b)$ at 775—790 cm^{-1}. The spectrum of the aquaoxalato-complex[14] $[Mo_2O_5(C_2O_4)_2(OH_2)_2]^{2-}$ shows a group of bands at 960s, 920vs, 860m, and *ca.* 780—800s cm^{-1} (the last represented by a broadening of the oxalato-band). The first, second, and fourth of these bands would seem to correspond with the absorptions characteristic of the nitrilotriacetato-complexes (Table 1). The *cis*-trioxo-fragments, $Mo(O_t)_2O_b$, of the nitrilotriacetato- and aquaoxalato-complexes are of closely similar geometry † (Table 2), but differences in their spectra may arise from coupling[2] of the $\nu(Mo-O_t)$, $\nu(Mo-O_b)$, and $\nu(Mo-O_l)$ modes. A cyclopentadienyl complex[16] formulated $[Mo_2O_5(\eta-C_5H_5)_2]$ is reported to give $\nu_{asym}(Mo-O_t)$ at 920s, $\nu_{sym}(Mo-O_t)$ at 898s and 850m, and $\nu_{asym}(Mo-O_b-Mo)$ at 770s cm^{-1}. The molecular geometry has not been determined, but the wavenumbers of the strong bands are close to those for the nitrilotriacetato-complex.

TABLE 2

Geometry of *cis*-trioxo-groups $Mo(O_t)_2O_b$

Complex	Distance/Å		Angle/°	
	$r(Mo-O_t)$	$r(Mo-O_b)$	O_bMoO_t	O_tMoO_t
$[Mo_2O_5(Hnta)_2]^{2-}$ [a]	1.68(1), 1.71(1)	1.880(1)	103.6 (0.2), 101.4 (0.2)	105.8 (0.3)
$[Mo_2O_5(C_2O_4)_2(OH_2)_2]^{2-}$ [b]	1.68(2), 1.70(2)	1.876(2)	103.95 (0.68), 100.95 (0.75)	106.5 (1.0)

[a] Ref. 12. [b] Values from ref. 14.

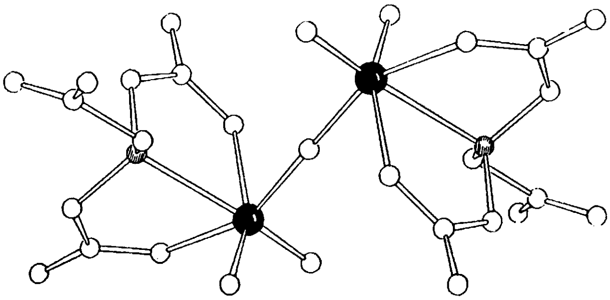

FIGURE 2 Co-ordination around the molybdenum centres in the complex anion $[Mo_2O_5(Hnta)_2]^{2-}$. Two of the three acetato-groups attached to the nitrogen (shaded) are co-ordinated, each through a single oxygen

The potentially tridentate diaminomonohydric alcohol 2-(3-aminopropylamino)ethanol (monoanion aae^-) might be expected to form a neutral complex with an Mo_2O_5 core, and in fact a compound (13) of composition $[Mo_2O_5(aae)_2]$ was obtained. It shows strong bands at 745, 825, 845, and 885 cm^{-1} in the Mo_2O_5 range. The structure of the compound is undetermined and the pattern of bands differs again from those of the nitrilotriacetato- and oxalato-complexes, but there seems no reason to doubt that the spectral bands result from an Mo_2O_5 core.

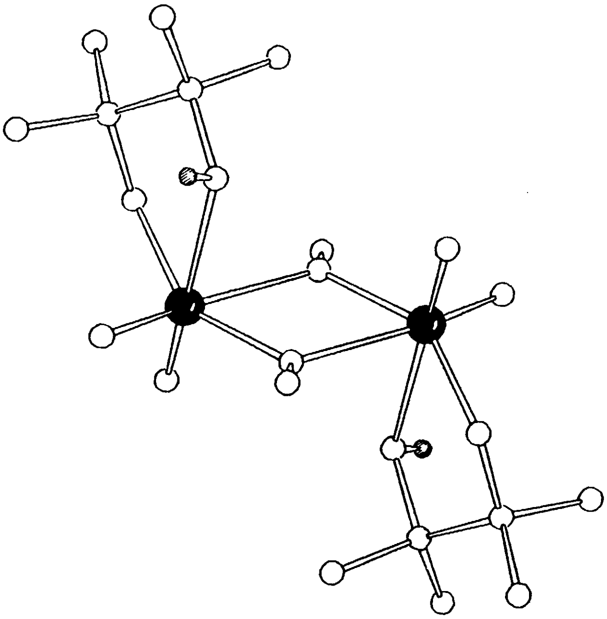

FIGURE 3 Co-ordination environment around the molybdenum centres in the compound $[\{MoO_2(Hpin)(OMe)\}_2]\cdot 2MeOH$, showing the double bridging by the two methoxy-groups. In the crystal there is extended intermolecular hydrogen bonding from the pinacolate protons (shaded) to the lattice methanol (which is not shown)

Class (*iv*).—Ligand-bridged structures may be assumed to exist when the ligand(s) would not otherwise complete six-co-ordination. The structures of the 2,2-dimethylpropane-1,3-diol (neopentyl glycol, dianion npg^{2-}) complex[17] $[\{MoO_2(npg)(OH_2)\}_2]$ (14) and the methanolate[12] (9), Figure 3, have now been established.

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* Triethanolamine has been shown (L. O. Atovmyan and O. N. Krasochka, *Chem. Comm.*, 1970, 1670) to function as a quadridentate ligand towards an MoO_2 core, so that nitrilotriacetic acid and triethanolamine differ in their ligancy.

† A comprehensive review has been made of molybdenum-oxygen bond lengths, and of bond orders derived therefrom (F. A. Schröder, *Acta Cryst.*, 1975, **B31**, 2294).

Bridging is provided in the former structure by one end of a chelating ligand, and in the latter case by a monofunctional ligand.

The $\mathrm{Mo{-}O_{lb}}$ bond lengths in these compounds are longer [(9), 2.00 and 2.22; (14), 2.01 and 2.22 Å] than $\mathrm{Mo{-}O_b}$ distances [(7), 1.90; (10), 1.88 Å]. In consequence, the $\mathrm{MoO_{lb}Mo}$ i.r. bands in the ligand-bridged compounds lie at lower wavenumbers [(9), 690 $\mathrm{cm^{-1}}$; (14), 644 $\mathrm{cm^{-1}}$; (10), 790 and 777 $\mathrm{cm^{-1}}$]. For this reason a compound $[\{\mathrm{MoO_2(tmoe)}\}_n]$ (15) obtained from the branched ligand 2-hydroxymethyl-2-methylpropane-1,3-diol (trimethylolethane, dianion $\mathrm{tmoe^{2-}}$), which shows no metal–ligand band above that at 635 $\mathrm{cm^{-1}}$, is considered to be a ligand-bridged complex. 2,2′-Oxydiethanol (diethylene glycol, dianion $\mathrm{deg^{2-}}$) forms a complex whose structure remains uncertain. Analyses agree closely with the formulation $[\{\mathrm{MoO_2(deg)}\}_n]$, for which ligand bridging would be inferred. However, the spectrum shows an otherwise unassigned strong band at 847 $\mathrm{cm^{-1}}$, which could arise from an $\mathrm{MoO_bMo}$ bridge, as from a formulation $[\mathrm{Mo_2O_5(Hdeg)_2}]$.

In no case is there evidence of ligand bridging by a vicinal diol, but a ligand-bridged structure does develop readily with neopentyl glycol, which is a 1,3-diol. This would indicate that a five-membered ring is best suited to simple chelation, and that lengthening of a potentially chelating chain, enabling attainment of an increased angle of bite [149° in (15), as compared with 71—76° in (1), (4), and (7)] is more favourable to development of ligand bridging.

From Table 1 it will be seen that the usual ranges ($\mathrm{cm^{-1}}$) within which characteristic i.r. bands lie are as follows: $\mathrm{MoO_2}$(*cis*-dioxo), $\nu(\mathrm{Mo{-}O_t})$ at 885—950; $\mathrm{Mo_2O_3}$, $\nu(\mathrm{Mo{-}O_t})$ at 920—950, $\nu(\mathrm{Mo{-}O_b})$ at 750—760; $\mathrm{Mo_2O_5}$, $\nu(\mathrm{Mo{-}O_t})$ at 900—930, $\nu(\mathrm{Mo{-}O_b})$ at 750—790, but with the possibility of intermediate bands. As a general conclusion, i.r. spectra can serve for the identification of $\mathrm{MoO_2}$ and $\mathrm{Mo_2O_3}$ cores, but cannot be used with confidence for $\mathrm{Mo_2O_5}$. An $\mathrm{MoO_{lb}Mo}$ band at 620—650 $\mathrm{cm^{-1}}$ (or higher in the special case of the methoxy-bridge) can provide evidence in support of ligand bridging, but it may not be unambiguous because of possible overlap with the $\nu(\mathrm{Mo{-}O_l})$ range.

EXPERIMENTAL

X-Ray analyses were carried out using an automatic four-circle diffractometer and normal computing procedures.

Preparations.—(*a*) *Reaction of the ligand with* $\mathrm{MoO_3}$ (*Schultheis method*).[10] Compounds (1)—(3), (5), and (6) of the $[\mathrm{MoO_2(HL)_2}]$ class, $[\{\mathrm{MoO_2(deg)}\}_n]$ (16), and $[\mathrm{Mo_2O_5(aae)_2}]$ (13) were obtained by heating molybdenum trioxide (2—4 g) with an excess (20 $\mathrm{cm^3}$) of the liquid ligand. Crystallisation of the complex occurred either on cooling or over a few days at 0 °C. Using diols it was suitable to maintain the reaction temperature at 180—190 °C for 5—10 min, in an oil-bath. Heating for longer, or at a higher temperature, led to decomposition and more difficult crystallisation. With aminoalcohols reaction occurred at *ca.* 120 °C, but a higher temperature was necessary to complete conversion into the desired product. In handling these products it was necessary to provide protection against atmospheric moisture. Examples of specific preparations are given. Analyses are shown in Table 3.

Bis(*butane*-2,3-*diolato*)*dioxomolybdenum*(VI) *bis*(*butane*-2,3-*diol*) (3). Molybdenum trioxide (5 g) was heated (190 °C) with butane-2,3-diol (50 $\mathrm{cm^3}$) for 5 min. The blue-black suspension was filtered and the white crystalline product separating over 2 d was washed with a little ethanol, diethyl ether, and light petroleum (b.p. 56—70 °C). The compound is distinctive among diol complexes in its low melting point (89 °C) and higher solubility in polar solvents. When pumped under high vacuum for 2 h at 90 °C it gave the yellow derivative (4), with weight loss through removal of solvate diol, and water, of 41.4% (calc.: 40.8%).

TABLE 3

Elemental analyses (%) with calculated values in parentheses

Compound [a]	C	H	Mo
$[\mathrm{MoO_2(Hpd)_2}]$	25.8	5.0	34.5
	(25.9)	(5.0)	(34.5)
$[\mathrm{MoO_2(Hbd)_2}]\cdot\mathrm{2H_2bd}$	39.5	7.7	19.4
	(39.5)	(7.8)	(19.7)
$[\mathrm{MoO_2(mea)_2}]$ [b]	19.8	5.2	38.6
	(19.4)	(4.9)	(38.7)
$[\mathrm{MoO_2(Hdea)_2}]$ [c]	28.6	6.2	28.2
	(28.6)	(5.95)	(28.6)
$[\mathrm{MoO_2(Hpin)_2}]$	39.5	7.1	26.9
	(39.8)	(7.2)	(26.5)
$[\mathrm{Mo_2O_3(bd)_2(Hbd)_2}]$	32.2	5.9	
	(32.3)	(5.7)	
$[\mathrm{Mo_2O_3(pin)_2(Hpin)_2}]$	40.4	6.9	26.9
	(40.8)	(7.1)	(27.2)
$\mathrm{Na_2[Mo_2O_5(Hnta)_2]\cdot 8H_2O}$ [d]	17.2	3.5	22.9
	(17.6)	(3.2)	(23.3)
$\mathrm{K_2[Mo_2O_5(Hnta)_2]\cdot 4H_2O}$ [e]	18.8	2.4	
	(18.4)	(2.55)	
$\mathrm{[NH_4]_2[Mo_2O_5(Hnta)_2]\cdot 4H_2O}$ [f]	19.5	3.8	25.5
	(19.5)	(3.8)	(25.9)
$[\mathrm{Mo_2O_5(aae)_2}]$	23.8	5.3	37.3
	(23.7)	(5.15)	(37.9)
$[\{\mathrm{MoO_2(Hpin)(OMe)}\}_2]\cdot\mathrm{2MeOH}$	31.3	6.5	30.8
	(31.2)	(6.5)	(31.2)
$[\{\mathrm{MoO_2(npg)(OH_2)}\}_2]$	24.8	4.9	38.2
	(24.2)	(4.8)	(38.7)
$[\{\mathrm{MoO_2(tmoe)}\}_n]$	25.2	4.1	38.2
	(24.4)	(4.1)	(39.0)
$[\{\mathrm{MoO_2(deg)}\}_n]$	21.0	3.6	40.8
	(20.7)	(3.45)	(41.4)

[a] pd = $\mathrm{C_3H_6O_2}$, bd = $\mathrm{C_4H_8O_2}$, mea = $\mathrm{C_2H_6NO}$, dea = $\mathrm{C_4H_9NO_2}$ pin = $\mathrm{C_6H_{12}O_2}$, nta = $\mathrm{C_6H_6NO_6}$, aae = $\mathrm{C_5H_{13}N_2O}$, npg = $\mathrm{C_5H_{10}O_2}$, tmoe = $\mathrm{C_5H_{10}O_3}$, and deg = $\mathrm{C_4H_8O_3}$. [b] N, 11.2 (11.3%). [c] N, 8.4 (8.3%). [d] N, 3.5 (3.7). Na, 5.0 (5.6%); $\mathrm{H_2O}$: Mo = 3.8 : 1. [e] N, 3.6 (3.6%). [f] N, 7.2 (7.7%).

The complex (13) *from* 2-(3-*aminopropylamino*)*ethanol*. Molybdenum trioxide (3 g) was heated slowly with the ligand (20 $\mathrm{cm^3}$). There was initial reaction at 110—120 °C and as a dark intermediate product redissolved the temperature was slowly raised to 150 °C for a few minutes. A stainless-steel capsule of 4A molecular sieve pellets was placed in the filtered liquid. Crystallisation of the white complex occurred over 1 week. In this preparation it was necessary to avoid more concentrated solutions or more rapid heating. This causes rapid precipitation of a less pure product, and at *ca.* 160 °C complete conversion into a yellow product occurs.

(*b*) *Ligand exchange*. μ-*Oxo-bis*{*oxo*[*pinacolato*(1 −)][*pinacolato*(2 −)]*molybdenum*(VI)} (7). Pinacol (2.5 g) was stirred with bis(ethylene glycolato)dioxomolybdenum (1) (1 g) in dry ethanol (15 $\mathrm{cm^3}$) and the temperature raised to

40—50 °C to complete the reaction. The yellow compound was recrystallised from acetonitrile.

The trimethylol complex $[\{\mathrm{MoO_2(tmoe)}\}_n]$ (15). An intimate mixture of molybdenum(VI) acetylacetonate[18] (1 g) and trimethylolethane (0.4 g) was heated to 120 °C for 10 min. After removing the acetylacetone under vacuum the residue was crushed and extracted with small quantities of ethanol.

(*c*) *Reaction with ligand* (*nta*) *in aqueous solution. Disodium μ-oxo-bis*{cis-[*nitrilotriacetato*(2−)]*dioxomolybdate*-(VI)}-*water* (1/8), (10). Molybdenum trioxide, sodium hydroxide, and nitrilotriacetic acid (10 mmol of each) were dissolved in water (20 cm^3) and the solution allowed to evaporate at room temperature. The crystals were washed with a little 0.1 mol dm^{-3} hydrochloric acid and dried between filter paper. The ammonium salt (12) was obtained similarly from equivalent proportions of ammonium molybdate and nitrilotriacetic acid.

Dipotassium μ-oxo-bis[*aquaoxalato*-cis-*dioxomolybdate*(VI)]. This salt, for which a preparation has not been reported,[14] crystallised from a solution of potassium hydroxide, molybdenum trioxide, and oxalic acid (10 mmol of each in 20 cm^3). *X*-Ray precession photographs of single crystals established the identity of cell parameters and space group with those of the earlier reported complex.

(*d*) *Conversion from the ' yellow pinacolate '* (7). *Dioxobis*-[*pinacolato*(1−)]*molybdenum*(VI) (8). A solution of (7) in ethanol was allowed to evaporate. The (dark blue) mother-liquor was poured off and the white crystals washed with small quantities of solvent. Under azeotropic distillation with benzene (8) reconverts into (7). The weight loss through elimination of water at 50 °C under high vacuum was 2.6%.

Di-μ-methoxy-bis{cis-*dioxo*[*pinacolato*(1−)]*molybdenum*-(VI)}-*methanol* (1/2), (9). Compound (7) (0.1 g) was dissolved in dry methanol (3 cm^3) and allowed to crystallise in a small flask, initially open to the air for 10—15 min. The colourless elongated crystals turn blue on exposure to air and light after removal from the mother-liquor.

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